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| <p>(54) Title: DETERGENT COMPOSITIONS COMPRISING CATIONIC SURFACTANT AND PROCESS FOR MAKING THE COMPOSITION</p> <p>(57) Abstract</p> <p>The present invention concerns a granular detergent composition or composition comprising anionic surfactant, at least 20 % by weight of water-soluble cationic surfactant, and less than 10 % by weight of anionic polymer wherein the molar ratio of anionic surfactant to cationic surfactant is less than 1:1, preferably less than 0.5:1. Another aspect of the present invention is a process for making the composition or component comprising the steps of: (i) mixing an aqueous solution comprising water-soluble cationic surfactant, anionic surfactant, and less than 10 % by weight of anionic polymer, (ii) drying the mixture to form a concentrated solution having a solids level of at least 50 % by weight, and (iii) granulating the concentrated solution; wherein the cationic surfactant is at a level of at least 20 % by weight of the composition or component and the molar ratio of anionic surfactant to cationic surfactant is less than 1:1.</p> | | |

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DETERGENT COMPOSITIONS COMPRISING CATIONIC SURFACTANT AND
PROCESS FOR MAKING THE COMPOSITION

The invention relates to granular detergent compositions comprising cationic surfactant and anionic surfactant.

Water-soluble cationic surfactants are commercially available as aqueous solutions, typically up to 35% or 40% active (by weight). However any attempts to granulate these aqueous solutions result in granular components having low cationic surfactant content.

EP-A 000 225, published on 10th January 1979, discloses compositions comprising water-soluble cationic surfactant and anionic surfactant. The surfactants are combined together with other detergent ingredients, such as builders, in a crutcher mix and spray-dried. It is an

essential feature that there is a molar excess of anionic surfactant over cationic surfactant. The examples disclose up to a maximum of about 8% by weight of cationic surfactant in the spray dried component.

Attempts to increase cationic surfactant content of granular compositions by first concentrating the aqueous solution have proved very difficult because viscous gel phases of concentrated cationic surfactant make further processing extremely difficult on a commercial scale.

The present invention aims to provide granular detergent components or compositions having a higher level of water-soluble cationic surfactant than prior art components.

This is achieved by mixing small amounts of anionic surfactant with the aqueous solution of the cationic surfactant, and subsequently drying and granulating, either simultaneously or sequentially. The addition of the anionic surfactant permit more concentrated cationic solutions to be processed without entering a viscous gel phase. Consequently more concentrated granular surfactant components or compositions can be produced.

Summary of the Invention

The present invention concerns a granular detergent composition or component comprising anionic surfactant, at least 20% by weight of water-soluble cationic surfactant, and less than 10% by weight of anionic polymer wherein the molar ratio of anionic surfactant to cationic surfactant is less than 1:1, preferably less than 0.5:1.

The granular detergent composition or component preferably comprises the cationic surfactant at a level of at least 30% by weight of the composition or component, and the anionic surfactant at a level of from 1% to 20% by weight of the composition or component.

Optionally the granular detergent composition or component further comprises from 10% to 69% by weight of a detergent builder selected from the group consisting of aluminosilicate, silicate, carbonate, citrate, phosphate or mixtures thereof.

A highly preferred granular detergent composition or component is substantially free of anionic polymer, and comprises:

- (a) from 35% to 50% by weight of water-soluble cationic surfactant;
- (b) from 1% to 5% by weight of anionic surfactant; and
- (c) from 40% to 60% by weight of sodium

aluminosilicate.

Another aspect of the present invention is a process for making the composition or component comprising the steps of

- (i) mixing an aqueous solution comprising water-soluble cationic surfactant, anionic surfactant, and less than 10% by weight of anionic polymer;
- (ii) drying the mixture to form a concentrated solution having a solids level of at least 50% by weight, and
- (iii) granulating the concentrated solution;

wherein the cationic surfactant is at a level of at least 20% by weight of the composition or component and the molar ratio of anionic surfactant to cationic surfactant is less than 1:1.

Optionally a suds suppressing agent is added to the mixing step (i).

The drying step may be carried out by means of an evaporation step, and that the granulating step is subsequently carried out by mixing the concentrated solution with a detergent builder selected from the group consisting of aluminosilicate, silicate, carbonate, citrate, phosphate or mixtures thereof.

Alternatively the drying and granulating steps may be carried out simultaneously, preferably by means of spray drying.

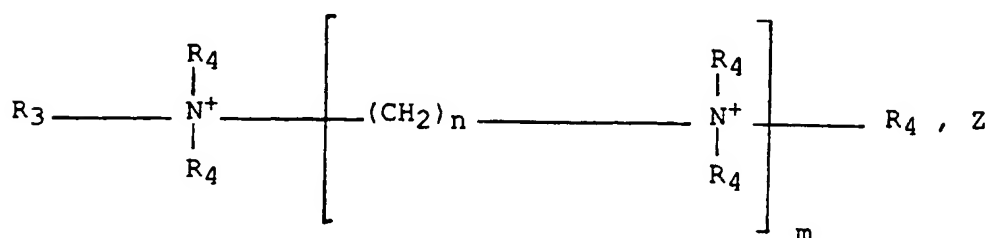
Detailed Description of the Invention

The cationic surfactant component of the composition is water-soluble. By water solubility we refer in this context to the solubility of cationic surfactant in monomeric form, the limit of solubility being determined by the onset of micellisation and measured in terms of the critical micelle concentration (CMC). The cationic surfactant should thus have a CMC for the pure material greater than about 200ppm and preferably greater than about 500ppm, specified at 30°C and in distilled water (Critical Micelle Concentrations of Aqueous Surfactant Systems, P. Mukerjee and K.J. Mysels, NSRDS-NBS, (1971)).

Useful cationic surfactants include water-soluble quaternary ammonium compounds of the form $R_1R_2R_3R_4N^+X^-$, wherein R_1 is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and R_2 , R_3 and R_4 are each C_1 to C_7 alkyl, or hydroxyalkyl, preferably methyl; X^- is an anion, e.g. chloride. Examples of such quaternary ammonium compounds include C_{12-14} alkyl trimethyl ammonium chloride, C_{12-14} alkyl dimethyl ethoxy ammonium chloride and cocalkyl

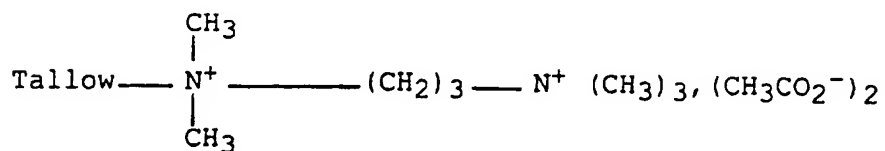
trimethyl ammonium methosulfate. Other useful cationic surfactants are described in US Pat No. 4,222,905, Cockrell, issued Sept 16, 1990 and in US Pat No 4,239,659, Murphy, issued Dec. 16, 1980.

Another group of useful cationic compounds are the polyammonium salts of the general formula :

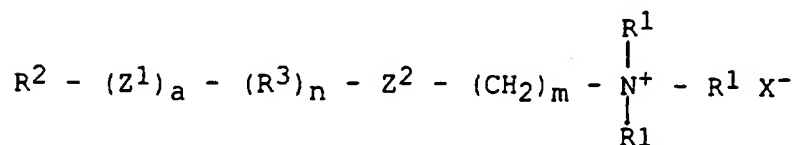


wherein R_3 is selected from C_8 to C_{20} alkyl, alkenyl and alkaryl groups; each R_4 is C_1 - C_4 alkyl; n is from 1 to 6; and m is from 1 to 3.

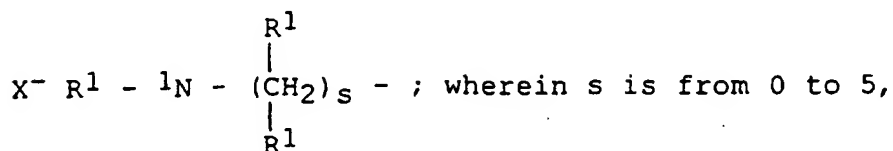
A specific example of a material in this group is :



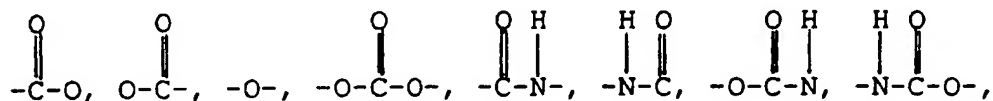
A further preferred type of cationic component, has the formula :



wherein R^1 is C_1 to C_4 alkyl; R^2 is C_5 to C_{30} straight or branched chain alkyl or alkenyl, alkyl benzene, or



R^3 is C_1 to C_{20} alkyl or alkenyl; a is 0 or 1; n is 0 or 1; m is from 1 to 5; Z^- and Z^2 are each selected from the group consisting of :

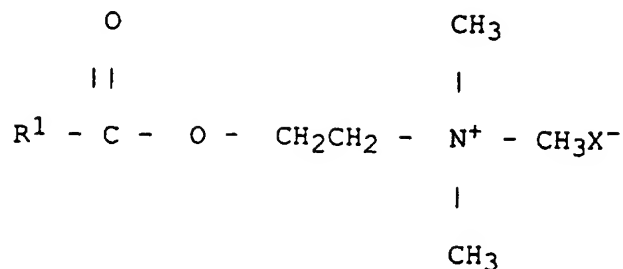


and wherein at least one of said groups is selected from the group consisting of ester, reverse ester, amide and reverse amide; and X is an anion which makes the compound water-soluble, preferably selected from the group consisting of amide, methyl sulfate, hydroxide, and nitrate preferably chloride, bromide or iodine.

In addition to the advantages of the other cationic surfactants disclosed herein, this particular cationic component is environmentally desirable, since it is biodegradable, both in terms of its long alkyl chain and its nitrogen containing segment.

Choline esters :

Preferred choline ester derivatives having the following formula :



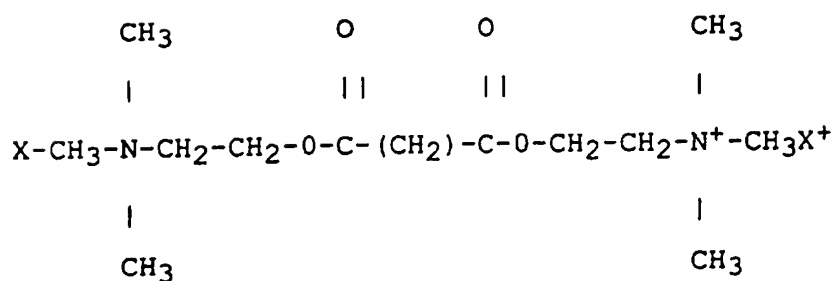
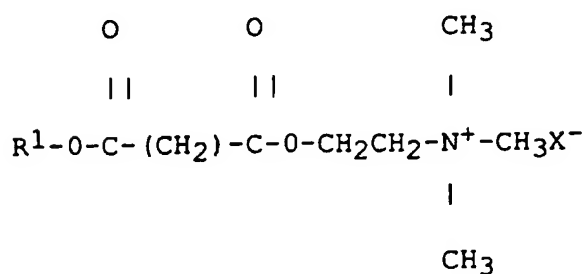
wherein R is a C₅ to C₃₀ straight chain or branched chain alkyl or alkenyl, group and X is an anion, which makes the compound at least water-dispersible, preferably selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, preferably methyl sulfate, chloride, bromide or iodide,

as well as those wherein the ester linkage in the above formula is replaced with a reverse ester, amide or reverse amide linkage.

Particularly preferred examples of this type of cationic surfactant include stearoyl choline ester quaternary ammonium halides (R¹=C₁₇ alkyl), palmitoyl choline ester quaternary ammonium halides (R¹=C₁₅ alkyl), mystiroyl choline ester quaternary ammonium halides (R¹=C₁₃ alkyl), lauroyl choline ester ammonium halides (R¹=C₁₁ alkyl), as well as coconut and tallow choline ester quaternary

ammonium halides ($R^1 = C_{15}-C_{17}$ alkyl and $C_{19}-C_{21}$ alkyl, respectively).

Additional preferred cationic components of the choline ester variety are given by the structural formulas below, wherein p may be from 0 to 20.



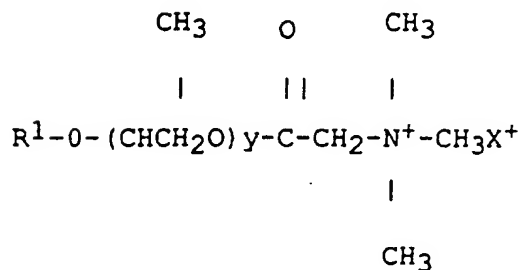
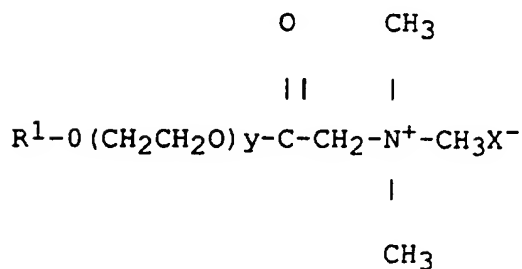
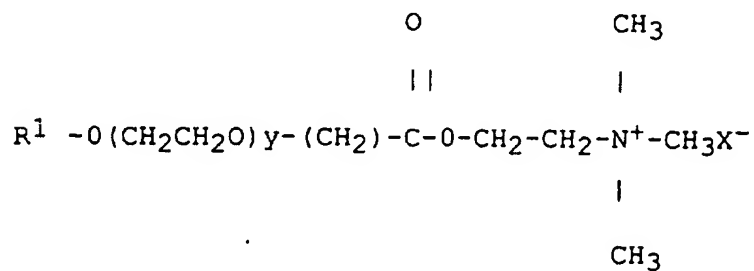
The preferred choline-derivative cationic substances, discussed above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid

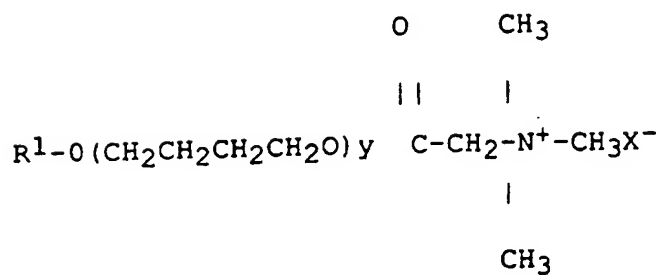
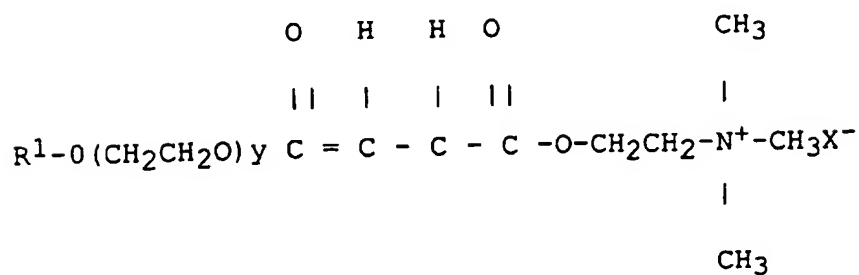
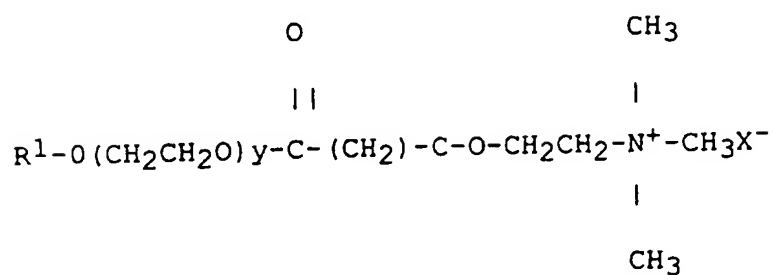
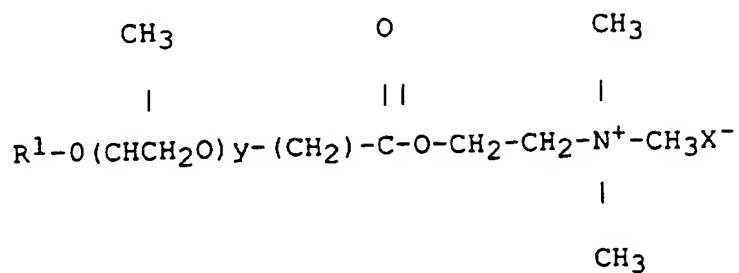
catalyst. The reaction product is then quaternized with a methyl halide, forming the desired cationic material.

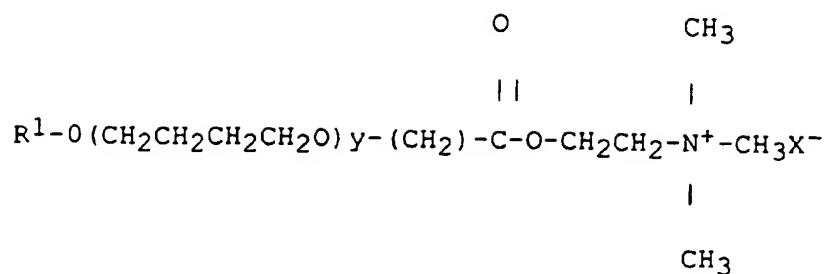
The choline-derived cationic materials may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then used to quaternize.

Trimethylamine, forming the desired cationic component.

Other suitable choline esters for use herein have the formula:







wherein t is 0 or 1, y is from 1 to 20, and R and X are as defined above.

Anionic Surfactant

The anionic surfactant component of the present invention include water-soluble salts of the higher fatty acids, i.e., "soaps". This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkyl benzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C₁₁-C₁₃ LAS.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the

alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; watersoluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety.

Also considered as anionic surfactants useful in the present invention are hydrotropes such as aryl sulphonates. Preferred are sodium or potassium salts of benzene, toluene, xylene or cumene sulphonate.

Suds Suppressing Agent

A suds suppressing agent is useful in the present invention as a process aid, to control suds at the stage of mixing the cationic surfactant solution with the anionic surfactant.

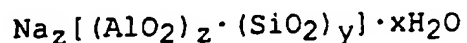
A wide variety of materials may be used as suds suppressing agents such as monocarboxylic fatty acids and their soluble salts, high molecular weight hydrocarbons such as paraffin, fatty acid esters, fatty acid esters of monovalent alcohols, aliphatic C1-C40 ketones, N-alkoxylated amino triazines, propylene oxide, and monstearyl phosphates and phosphate esters. Another preferred category of suds suppressing agents comprises silicone suds suppressors.

This category includes the use of polyorganosiloxane oils, such as polydimethyl siloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well-known in the art and are, for example, disclosed in US-A 4 265 779, issued May 5th 1981. Other silicone suds suppressors are disclosed in US-A 3 455 839 and German Patent Application DE-A 21 24 526.

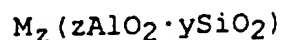
Powders

Many powders are suitable for use in the granulation step of the present process. Preferred powders for use in the process and compositions of the present invention are compatible detergent builder or combination of builders or powder.

The detergent compositions herein can contain crystalline aluminosilicate ion exchange material of the formula



wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.4 and z is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula



wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO_3 hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 1 to 10 microns is preferred.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of

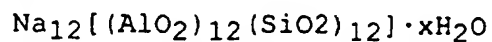
CaCO₃ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains

Ca⁺⁺/gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

The amorphous aluminosilicate ion exchange materials usually have a Mg⁺⁺ exchange of at least about 50 mg eq. CaCO₃/g (12 mg Mg⁺⁺/g) and a Mg⁺⁺ exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al.,

issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula



wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

The granular detergents of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Citric acid and, in general, any other organic or inorganic acid may be incorporated

into the granular detergents of the present invention as long as it is chemically compatible with the rest of the agglomerate composition.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, citrates, silicas and polyhyroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio

of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. The compositions made by the process of the present invention does not require excess carbonate for processing, and preferably does not contain over 2% finely divided calcium carbonate as disclosed in U.S. Pat. No. 4,196,093, Clarke et al., issued Apr. 1, 1980, and is preferably free of the latter.

Softening Clay

Softening clay is a particularly useful component which may be optionally incorporated into the compositions of the present invention. When used, the clay may be incorporated into the cationic surfactant containing particle of the present invention, however it is preferred that the clay is incorporated into a particle separate from the cationic surfactant. The cationic surfactant containing particles and the clay containing particles may then be mixed together, usually with other particulate components comprising conventional detergent ingredients to give a finished commercial laundry detergent product.

Softening clays may be either unmodified or organically modified. Those clays which are not organically modified can be described as expandable, three-layered clays, i.e., aluminosilicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100g. of clay and

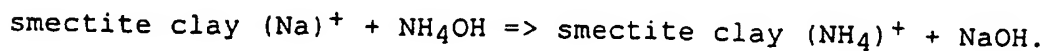
preferably at least 60 meq/100 g. of clay. The starting clays for the organically modified clays can be similarly described. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen, or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays that can be broadly differentiated on the basis of the numbers of octahedral metal-oxygen arrangements in the central layer for a given number of silicon-oxygen atoms in outer layers. A more complete description of clay minerals is given in "Clay Colloid Chemistry" by H. van Olphen, John Wiley & Sons (Interscience Publishers), New York, 1963. Chapter 6, especially pages 66-69.

The family of smectite (or montmorillonoid) clays includes the following trioctahedral minerals: talc; hectorite; saponite; sauconite; vermiculite; and the following dioctahedral minerals: prophyllite; montmorillonite; volchonskoite and nontronite.

The clays employed in these compositions contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, and lithium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is

predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation :



Since in the foregoing equilibrium reaction, an equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq/100g). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration, or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971).

The cation exchange capacity of a clay material relates to such factors as the expandable properties of the clay, the charge of the clay (which in turn is determined at least in part by the lattice structure), and the like. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. of kaolinites to about 150 meq/100 g., and greater, for certain smectite clays.

Preferred smectite-type clays are sodium montmorillonite, potassium montmorillonite, sodium hectorite and potassium

hectorite. The clays used herein have a particle size range of up to about 1 micron.

Any of the clays used herein may be either naturally or synthetically derived.

Examples

In the following examples

Cationic surfactant is C12-14 alkyl dimethyl hydroxyethyl ammonium chloride

Sodium (C12-14) alkyl ether (3) sulphate is the sodium salt of a C12-14 ethoxylated alcohol having an average of 3 moles of ether per mole.

Suds Suppressing Agent is poly dimethyl siloxane (85%) and hydrophobic silica (15%)

The following composition was made :

| | % by weight |
|---|-------------|
| Cationic Surfactant | 40 |
| Sodium (C12-14) alkyl sulphate | 1.6 |
| Sodium (C12-14) alkyl ether (3) sulphate | 0.4 |
| Zeolite A (hydrated) | 54.9 |
| Suds Suppressing Agent | 0.1 |
| Water | 3 |

Example 1

The above composition was prepared by mixing a 40% aqueous solution of the cationic surfactant with a 79% aqueous

paste of the mixture of anionic surfactants, and with the antifoam. The mixture was then evaporated to form a 60% cationic surfactant active paste. The paste was fed into a high shear mixer (a Loedige CB®) where it was granulated with the Zeolite A. The resulting granules were further treated in a low shear mixer (a Loedige KM®) and subsequently dried in a fluid bed dryer to a moisture level of 3% (free) water.

Example 2

The above composition was prepared by mixing a 40% aqueous solution of the cationic surfactant with a 79% aqueous paste of the mixture of anionic surfactants. The Zeolite A was also added to the mixture and a homogeneous crutcher mix formed. The crutcher mix was then spray dried using hot air in a conventional counter-current spray dry tower to give the finished granular composition.

Comparative Example A

A 40% aqueous solution of the cationic surfactant was fed into a high shear-mixer (Loedige CB®) and agglomerated with a fixed amount of Zeolite A powder. The feed was stopped just before over-agglomeration occurred (the point where the liquid level exceeds the capacity of the powder,

leading to the formation of an un-processable 'dough'). The resultant wet agglomerate was then dried in a fluid-bed dryer giving a product with the following composition :-

| | % by weight |
|--------------------------------|-------------|
| Cationic Surfactant | 15 |
| Sodium (C12-14) alkyl sulphate | - |
| Sodium (C12-14) alkyl ether | - |
| (3) sulphate | |
| Zeolite A (hydrated) | 82 |
| Water | 3 |

This particle is not suitable for inclusion in 'compact-type' products due to the low cationic surfactant activity.

Comparative Example B

A 40% aqueous solution of the cationic surfactant was dried by evaporation to form a 60% cationic surfactant active paste. The paste became a highly viscous gel and no further useful processing was possible.

CLAIMS

1. A granular detergent composition or component comprising anionic surfactant, water-soluble cationic surfactant, and less than 10% by weight of anionic polymer characterised in that the cationic surfactant is at a level of at least 20% by weight of the composition or component and the molar ratio of anionic surfactant to cationic surfactant is less than 1:1.
2. A granular detergent composition or component according to claim 1 wherein the cationic surfactant is at a level of at least 30% by weight of the composition or component, and the anionic surfactant is at a level of from 1% to 20% by weight the composition or component and the molar ratio of anionic surfactant to cationic surfactant is less than 0.5:1.
3. A granular detergent composition or component according to claim 2, further comprising from 10% to 69% by weight of a detergent builder selected from the group consisting of aluminosilicate, silicate, carbonate, citrate, phosphate or mixtures thereof.

4. A granular detergent composition or component according to claim 3, which is substantially free of anionic polymer, comprising:

- (a) from 35% to 50% by weight of water-soluble cationic surfactant;
- (b) from 1% to 5% by weight of anionic surfactant; and
- (c) from 40% to 60% by weight of sodium aluminosilicate.

5. A process for making the composition or component comprising the steps of

(i) mixing an aqueous solution comprising water-soluble cationic surfactant, anionic surfactant, and less than 10% by weight of anionic polymer

(ii) drying the mixture to form a concentrated solution having a solids level of at least 50% by weight, and

(iii) granulating the concentrated solution;

characterised in that

the cationic surfactant is at a level of at least 20% by weight of the composition or component and the molar ratio of anionic surfactant to cationic surfactant is less than 1:1.

6. A process according to claim 5 wherein a suds suppressing agent is added to the mixing step (i).

7. A process according to either of claims 5 or 6 wherein the drying step is carried out by means of an evaporation step, and that the granulating step is subsequently carried out by mixing the concentrated solution with a detergent builder selected from the group consisting of aluminosilicate, silicate, carbonate, citrate, phosphate or mixtures thereof.

8. A process according to claim 5 wherein the drying and granulating steps are carried out simultaneously, preferably by means of spray drying.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15548

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 1/65, 17/06

US CL : 242/110, 134, 547, 550, 174

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 242/110, 134, 547, 550, 174

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search terms: granule# or granular, cationic, anionic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | US, A, 4,347,168 (MURPHY ET AL.) 31 August 1982, col. 2, lines 40-65; col. 4, line 63 - col. 5, line 38; col. 6, lines 19-62; col. 8, lines 62-66; col. 9, lines 58-65; col. 11, lines 6-19; col. 12, lines 10-51; Examples 6 and 12. | 1-8 |
| A | US, A, 4,259,215 (MURATA ET AL.) 31 March 1981, claims 1-9. | 1-8 |
| A | US, A, 4,338,204 (SPADINI ET AL.) 06 July 1982, col. 2, line 35 - col. 3, line 39. | 1-8 |
| A | US, A, 4,430,244 (BROZE ET AL.) 07 February 1984, col. 2, lines 56-64; col. 8, lines 46-58. | 1-8 |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | |
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| * Special categories of cited documents: | * T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention |
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| * L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | * A* | document member of the same patent family |
| * O* document referring to an oral disclosure, use, exhibition or other means | | |
| * P* document published prior to the international filing date but later than the priority date claimed | | |

Date of the actual completion of the international search

16 FEBRUARY 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/15548

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | US, A, 5,071,594 (BORLAND ET AL.) 10 December 1991, col. 3, line 24 - col. 4, line 14; Examples 35-40. | 1-8 |

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